

## Hydrodesulfurization of Bituminous Coal Chars

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One of the products of many of the coal conversion processes now under development is a porous semi-coke or char. In the course of work under Project COED (Char Oil Energy Development), carried out by FMC Corporation under sponsorship of the Office of Coal Research of the U. S. Department of the Interior, a process has been developed for the desulfurization of such chars. The desulfurization of char proceeds in several chemical steps. These are:

1. Reaction of sulfur species with hydrogen to form  $H_2S$ .
2. Diffusion of the  $H_2S$  from the char into the bulk gas.
3. Absorption of the gaseous  $H_2S$  by an acceptor.
4. Regeneration of the acceptor with production of by-product sulfur.

This paper treats studies of the first two steps. A subsequent paper describes the acceptance of  $H_2S$  under process conditions and the regeneration of the  $H_2S$  acceptor.

Work by Consolidation Coal Company<sup>(1,5)</sup> established that high-temperature hydrogenation is effective in desulfurizing chars from Pittsburgh-seam coals. Equilibrium isotherms for the exchange of sulfur between gaseous hydrogen sulfide and sulfur in these chars were measured. These isotherms indicated that equilibrium concentrations of 0.5 percent hydrogen sulfide or less could be expected. However, kinetic data and data on the effect of process variables such as pressure, temperature and gas velocity were not available. Such data were needed to determine the technical and economic feasibility of incorporating char desulfurization into the COED concept. For these reasons, this experimental program was undertaken to:

1. Demonstrate the technical feasibility of desulfurizing COED chars by a high-temperature hydrogenation process.
2. Identify the important process variables associated with this process step.
3. Obtain kinetic data for this process.

#### Experimental Apparatus

The experimental system is shown in Figure 1. The reactor was a two-foot section of 3/4-inch, schedule 40, type 316, stainless steel pipe. A 22-inch long thermowell of 1/4-inch O.D. stainless steel tubing ran up the center of the reactor. A 14-mesh screen was welded to the thermowell about one foot from the bottom of the reactor to support the char bed.

The reactor was mounted vertically in a one-foot-long tubular electric furnace (Basic Products Corp., Model MK70). Power to the

furnace was controlled by an autotransformer. The temperature was monitored by a chromel-alumel thermocouple. Reactor pressure was measured with a gauge. Off gases were metered through a rotameter and a wet test meter in series, and vented to the atmosphere. Gas flow rate and reactor pressure were controlled with needle valves (1) and (4).

#### Run Procedure

A plug of ceramic wool was positioned on top of the support screen. Then a weighed sample char, from which the minus 200-mesh particles had been sieved, was charged on top of the wool plug. A second ceramic wool plug was placed on top of the bed to prevent any carryover of fines into the rest of the system.

The reactor was positioned in the furnace to locate the char bed in the center of the heated zone. The thermocouple was inserted into the thermowell to measure the temperature of the bed.

The furnace and reactor were brought up to reaction temperature with nitrogen being purged through the reactor. After the desired temperature had been reached, hydrogen was introduced into the system. This marked the start of the run. Gas flow rate and pressure were then adjusted to the desired levels. These adjustments took less than two minutes. For the two- and five-minute runs, the hydrogen rate was preset at room temperature, so that the desired conditions were attained at temperature. After the run, the reactor was dismantled, and the treated char weighed and analyzed for weight percent sulfur.

Char was originally analyzed using the standard Eschka method. Subsequently, analyses were made using an X-ray emission (XRS) method in order to expedite operations. Analyses of the off gas were attempted, but consistent results were not obtained.

Deviations between the two methods were random as to sign, and were within the combined precision of the two methods. The precision of the Eschka method is  $\pm 0.1$  percent sulfur; that of the XRS technique,  $\pm 0.05$  percent.

The experimental program was carried out using char from Crown (Illinois No. 6-seam) coal. The char had been processed in the COED process development unit at a maximum temperature of 1600°F(2). Tables I to III are compilations of the properties of this char before and after treatment with hydrogen at 1600°F. The sulfur content of the untreated char increased with decreasing char particle size, as did the ash content. This is presumably the result of a similar distribution of sulfur and ash in the crushed coal.

The distribution of sulfur between pyritic and organic forms is worthy of note. About seventy percent of the sulfur in this char was present as "organic" sulfur. This distribution is reasonably typical of coals of the Illinois No. 6-seam. The "pyritic" sulfur originally present in the coal has been converted, during pyrolysis, to ferrous sulfide, and/or pyrrhotite ( $\text{Fe}_7\text{S}_8$ ). The pyrite in the raw coal from which the char was derived was present as small particles from 3 to 25 microns in diameter. Microscopic examination showed that the bulk of the pyrite was present in fine veins of varying widths. The remainder was distributed, more or less at random, through the coal.

The desulfurization treatment had little effect on the properties of the char other than reducing the sulfur and moisture contents. Most differences in properties between treated and untreated chars are within the range of sampling error.

Because of the dependence of total sulfur content, and presumably also of inorganic/organic sulfur ratio on particle size, feed preparation and sampling were critical. Run feeds were prepared from large samples by multiple passes through a sample splitter. In general, only char from which the minus 200-mesh fraction had been removed was used. Within any group of feed samples from a parent batch, the standard error due to sampling was  $\pm 0.13$  weight percent sulfur. From one master batch to another, far larger deviations were encountered.

## RESULTS

Initial work was directed along lines suggested by preceding investigations(1,5). The variables investigated were:

1. Temperature.
2.  $H_2S$  concentration.
3. Char particle size.
4. Scale-up.

### Effect of Temperature

A graph of log percent sulfur removed from the char versus reciprocal temperature is shown in Figure 2. Runs were made at various temperatures at constant conditions of pressure, time and weight-space velocity (lb.  $H_2$  per hr. per lb. char). These data clearly do not have the significance of a normal Arrhenius plot. They merely serve to point out that the rate of desulfurization is not particularly influenced by temperature at temperatures above 1600°F. At lower temperatures, the rate of desulfurization decreases.

### Effect of Hydrogen Sulfide

It has been reported(1) that  $H_2S$  concentration is the most important variable in the desulfurization of char with hydrogen. Consequently, two hydrogen sulfide-hydrogen mixtures were prepared with  $H_2S$  contents of 1.6 and 3.2 volume percent. The results from runs using these mixtures are shown in Table IV. Runs made with pure hydrogen are presented for comparison. It is evident that 1.4 percent  $H_2S$  is sufficient to inhibit the reaction severely and that 3.2 percent  $H_2S$  may be enough to reverse the reaction. Previous work showed that as little as 0.2 percent hydrogen sulfide can cause a 10 to 40 percent reduction in desulfurization rate.

### Effect of Particle Size

In the case of bulk diffusional mechanisms, reactant particle size is an important variable. To determine the effect of particle size, a sample of plus 28-mesh char ( $d > 0.0234$  in.) was sieved from COED char. A part of this sample was then ground with a mortar and pestle to pass through 200 mesh ( $d < 0.0029$  in.). Both samples were given identical desulfurization treatments.

The results from the runs with sized char are given in Table V. At all conditions, differences in residual sulfur between the plus 28- and the minus 200-mesh char are within experimental uncertainties. Thus, the desulfurization process appears to be independent of particle size. Runs made with the entire size distribution show less residual sulfur than equivalent runs with sized char. This may be due to the nature of the sulfur in the plus 28-mesh fraction used for the sized runs.

#### Effect of Scale-Up

Eighty percent desulfurizations was achieved in the 3/4-inch reactor system at 1600°F., 115 psia, weight-space velocity ( $S_w$ ) of 0.9, and 1-hour reaction times for 10-gm. char charges. A larger reactor of 2-inch schedule 80 stainless steel pipe was fabricated and replaced the 3/4-inch reactor in the desulfurization system shown in Figure 1.

The reactor was run with a charge of 100 grams of char at weight-space velocities of 0.29 to 0.65. Reaction times of 3 to 6 hours were required to achieve 70 to 80 percent desulfurization. Since the space velocity had been preserved in these runs, the long reaction times needed were surprising. Because this result suggested that the system was more complex than expected, an extensive experimental program was formulated.

The expanded program was formulated in terms of the variables of superficial velocity,  $U$ , volumetric space velocity,  $S_v$ , and pressure,  $P$ . The program was originally planned as a  $2^3$  factorial design with a midpoint. It turned out, however, that it was impossible to achieve two of the design conditions.

The experimental design is shown in Table VI. Runs were made for time periods of 2, 5, 15, 30, 45, and 90 minutes. A number of replicates were made.

The results of the expanded series of experiments are presented in Figure 3 as percent residual sulfur versus time. Some general conclusions that can be drawn from these figures are:


1. The most significant variable in terms of the shape and position of the curves is bed height (+ $U$ , - $S_v$  diagonal). Curves 1, 2, 4, 5 and 7 on Figure 3 ( $H = 0.158$  ft.) are similar but differ significantly from curves 3 and 6 ( $H = 0.632$  ft.).
2. Three regimes of desulfurization seem to exist:
  - a. An almost instantaneous or "flash" desulfurization to 40 to 60 percent residual sulfur in the shallow beds (Runs 1, 2, 4, 5 and 7) and 60 to 70 percent residual sulfur in the deep beds (Runs 3 and 6). This flash takes place in less than two minutes.
  - b. A slower but still appreciable desulfurization rate to 10 to 15 percent residual sulfur. In the shallow beds this took about 45 minutes, while in the deep beds sulfur was still being evolved after 90 minutes.
  - c. Negligible desulfurization after a residual sulfur content of 10 to 15 percent is reached.

The data do not lend themselves readily to simple quantitative treatment. Indeed, in a complex, heterogeneous material such as coal char, it would be naive to expect otherwise. As is noted above, there appear to be several distinctly different regions of the curves.

## DISCUSSION OF RESULTS

### General

Much of the prior work on the desulfurization of cokes and coal chars has led to the conclusion that the reaction of hydrogen with sulfur in the char to form  $H_2S$  is a reversible process at high temperatures. In coals and presumably in coal chars as well, there are a wide variety of sulfur-containing species. These include the following types of chemical structures:

Inorganic Sulfur	$FeS, FeS_2$
Thiophenic Sulfur	
Mercaptans	$H-S-C$
Thioethers	$C-S-C$
Disulfides	$C-S-S-C$

Presumably some sulfur species are also adsorbed on the char surface. Because a variety of forms of sulfur are involved, no simple equilibrium expression can be used.

At a given total pressure, the equilibrium between  $H_2S$  and sulfur in char can be expressed as an "inhibition isotherm". This is a plot of the  $H_2S$  to hydrogen ratio in the gas versus sulfur concentration in the char. A typical isotherm for sulfur in a char from Arkwright coal (Pittsburgh-seam) is shown in Figure 4A.

Figure 4B is an inhibition isotherm for the desulfurization of COED char from Crown coal. This isotherm has been synthesized from the two measurements on inhibition of the reaction by  $H_2S$  (Table IV), and from an estimate of the  $FeS$  content based on the pyritic sulfur content of the feed coal. Region I corresponds to about 60 percent of the total sulfur in the form of relatively easily removable organic sulfur with equilibrium gas-phase concentrations in excess of 0.3 percent hydrogen sulfide. Region II corresponds to about 30 percent of the total sulfur in the form of inorganic sulfides ( $FeS$ ) with an equilibrium concentration of 0.3 percent hydrogen sulfide. Region III corresponds to about 10 percent of the total sulfur, in the form of organic sulfur, sulfate sulfur, and stable inorganic sulfides ( $CaS$ ), with equilibrium concentrations less than 0.3 percent hydrogen sulfide. The isotherm is probably not linear in this region since little of this sulfur is removed by prolonged hydrogenation.

The inhibition isotherm in Region I was assumed to be a straight line because only two experimental points were available. The shape of Figure 4A shows that this is a reasonable approximation. The equilibrium concentrations of hydrogen sulfide over COED char in

this region are significantly lower than those reported for char from Pittsburgh-seam coal (Figure 4A).

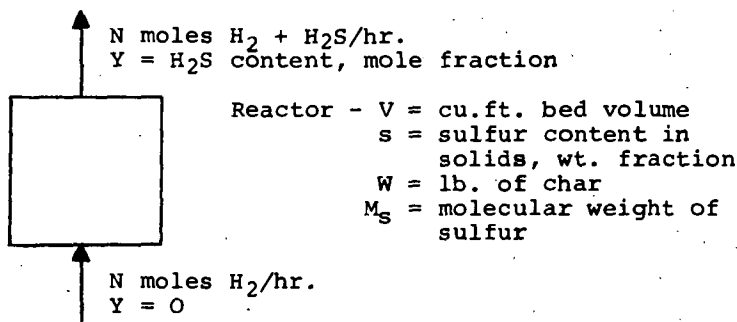
An equilibrium hydrogen-sulfide concentration of 0.3 percent was assumed in Region II. This figure was reported as the equilibrium concentration over FeS for Pittsburgh-seam char (Figure 4A) (1). The length of the FeS plateau (Region II) is fixed by the pyritic sulfur content of the char.

### Equilibrium Desulfurization

Given the existence of a reversible desulfurization reaction, the simplest model of the desulfurization process in a well-mixed bed is one assuming that the off gases are always in equilibrium with the sulfur in the bed of solids (3). The rate of desulfurization can be computed from the weight-space velocity of hydrogen through the bed and from the inhibition isotherm.

For the system defined below, where the flow rate of gases leaving the bed is  $N$  moles/hr. containing  $Y$  mole fraction  $H_2S$ , the rate of sulfur removal is  $NY$ .

Figure 5



Neglecting the sulfur content of the gases in the reactor at any instant,

$$-N \cdot Y = \frac{d}{dt} \left( \frac{s \cdot W}{M_s} \right) \quad (1)$$

for any arbitrary equilibrium expression relating  $s$  and  $Y$ ,

$$Y = f(s)$$

this expression may be integrated

$$t = \frac{W}{N \cdot M_s} \int_s^{s_0} \frac{ds}{f(s)}, \quad \text{where } t = \text{time of desulfurization, hr.} \quad (2)$$

The weight space velocity,  $S_w$ ,  $\frac{N \cdot M_{H_2}}{W}$ , so that Equation (2) simplifies to

$$t = \frac{1}{16 S_w} \int_s^{s_0} \frac{ds}{f(s)} \quad (3)$$

The following equilibrium relationship describes the inhibition isotherm in Figure 4B.

$$0 < s \leq 0.0035, \quad Y = 0.865 s \quad (4)$$

$$0.0035 < s \leq 0.0130, \quad Y = 0.0030 \quad (5)$$

$$0.0130 < s, \quad Y = 1.153 - 0.0118 s \quad (6)$$

The equilibrium desulfurization curves calculated from Equations (4), (5), and (6) for six of the conditions studied are plotted in Figure 6. Weight-space velocity is the only parameter here, so that two curves suffice for all six sets of data. The solid lines in Figure 6 are the predictions of the equilibrium model. The dashed lines indicate the approximate course of the data. This comparison shows quite clearly that the equilibrium model is only valid for the removal of the first forty to fifty percent of the sulfur in shallow beds. This would correspond to the first step or flash removal of sulfur mentioned previously.

#### Non-Equilibrium Desulfurization

Quite clearly, the equilibrium desulfurization model begins to break down when fifty to sixty percent of the sulfur has been removed from the char. Interestingly, this corresponds to the point at which most of the organic sulfur has been removed, and only ferrous sulfide and the "irremovable" sulfur remain in the char.

The reaction of the ferrous sulfide could possibly be limited by a number of diffusional steps as well as by the kinetics of the reaction itself. It will be recalled, however, that char particle size had little or no effect on the desulfurization rate. From this it is concluded that boundary layer diffusion, and bulk diffusion within the char structure are not important limiting steps. The very weak temperature dependence similarly suggests that chemical effects are not limiting.

While diffusion through the char is not limiting, it is certainly possible that diffusion through the shell of iron, which would surround a pyrite particle being desulfurized, might be a significant step in limiting the rate of reaction.

The following discussion is presented with the objective of showing that this explanation is qualitatively in accord with the observed desulfurization data. Quantitative verification of the model would require detailed knowledge of the distribution, shape, and size of the ferrous sulfide within the char. Such information is not available. Indeed, the information available concerning the pyrite in the coal is very preliminary and quite crude.

for the purposes of the initial analysis, the ferrous sulfide particles are assumed to be approximately spherical. Considering the very low partial pressure of  $H_2S$  over  $FeS$  under process conditions, a pseudo steady-state treatment should be quite adequate. The physical situation is illustrated in Figure 7. The governing differential equation is:

$$N_s = - \frac{4\pi r^2 \epsilon \mathcal{D}}{\tau^2} \left( \frac{dC}{dr} \right) \quad (7)$$

Where  $N_s$  is the rate of sulfur removal from the particle and  $C$  is the concentration of  $H_2S$  in the gas,  $\epsilon$  is the porosity,  $\mathcal{D}$  the diffusivity of  $H_2S$ , and  $\tau$  is the tortuosity in the diffusion barrier. In the case in question,  $C = 0$  at  $R_o$ , the outer surface of the particle, and

$$N_s \approx 4\pi R^2 \frac{dR}{dt} \left( \frac{\rho_{FeS}}{M_{FeS}} \right) \quad (8)$$

where  $\rho_{FeS}$  and  $M_{FeS}$  are the density and molecular weight of ferrous sulfide.

The pseudo steady-state allows us to treat the inner boundary as stationary, in integrating Equation (7). The integrated form can then be integrated in the time domain. The result is:

$$\frac{6MC_o^2 \epsilon \mathcal{D}}{\rho R_o^2} t = 1 - \left( \frac{R}{R_o} \right)^2 \left[ 3 - 2 \left( \frac{R}{R_o} \right) \right] \quad (9)$$

This solution is shown in Figure 8.

The stoichiometric variable of interest is the fraction unreacted. This fraction  $\frac{V}{V_o}$  is shown as a function of time in Figure 8 on arithmetic coordinates.

Figure 9 is a synthetic desulfurization experiment in which the first 55 percent of the sulfur is removed by the equilibrium mechanism, and the last 10 percent is "irremovable". The data for experimental condition 5 were superimposed by trial and error on the same ordinate. From the comparison of these points with the curve, it is apparent that the above explanation is consistent with the observed curve shape, particularly when one realizes that there will be a distribution of particle sizes in the char. It remains, now to determine whether the group  $(6 \epsilon t / R_o^2 \tau^2)$  is of reasonable magnitude.

In the real case, the time required to achieve 20 percent of the initial sulfur was 18 minutes, or 1080 sec. The porosity,  $\epsilon$ , should be about 0.6, and the tortuosity  $\tau$  is probably about 2. Taking  $R_o$  as 0.001 cm, one calculates a  $\mathcal{D}$  of  $\sim 10^{-3} \frac{\text{cm}^2}{\text{sec}}$ . This figure is reasonable if the diffusion through the reacted shell is in the Knudsen or transition regime.

The agreement may, however, be purely fortuitous. Further verification of the rate limiting step proposed here must await a test of the theory on a different high sulfur char, preferably one which has been processed through a COED unit.



### Conclusions

The equilibrium nature of the removal of the first 50 to 60 percent of the sulfur seems reasonably well established. There are fairly wide deviations which are probably a combination of internal diffusional effects and experimental technique. The procedure was designed for runs of 15 minutes or longer. Random errors would be expected to be high for the 2-minute and 5-minute runs. The inhibition isotherm for this char is only poorly established, but it is evident that this explanation is in general agreement with the data. The fact that this explanation fails at about 50 percent sulfur removal is also well established.

In the region of 50 to 90 percent sulfur removal, it is evident that elevated hydrogen pressure increases the rate of sulfur removal. This, however, is consistent with most possible rate-controlling steps. Bed depth is the only other variable that has a strong effect. In fact, bed depth is by far the most significant variable. Had the experiments been conducted in fixed beds, this would not have been so surprising. The experiments were carried out under conditions where the beds were fluidized, however. It appears, therefore, that there must have been a significant degree of reabsorption of sulfur within the four-inch bed to account for the observed results. This also raises the question as to whether the one-inch bed was truly a differential bed. If not, the observed rates may be slower than those achievable in the presence of an acceptor intimately mixed with the char. The results of experiments in the presence of  $H_2S$  acceptors suggest that this is so.

From the experimental results, it is apparent that a significant fraction of the sulfur content of Illinois No. 6 char, produced by the COED process, can be removed in contact times which are industrially realizable. It is equally evident that the hydrogen atmosphere becomes saturated with the addition of very little hydrogen sulfide. Hence, either vast amounts of hydrogen must be circulated at high temperature, or a material must be mixed with the char which will absorb  $H_2S$  at  $1600^\circ F.$  and at very low partial pressures. This latter approach seems by far the more feasible.

Nomenclature

C	Concentration (moles/cm <sup>3</sup> )
C <sup>0</sup>	Equilibrium Concentration
D	Diffusion Coefficient (cm <sup>2</sup> /sec)
f <sub>(s)</sub>	Inhibition isotherm (mole fraction)
M	Molecular weight - species indicated by subscript
N	Rate of flow (moles/sec)
N <sub>s</sub>	Rate of sulfur removal (moles/sec)
P	Pressure (psi)
r	radial distance (cm or microns)
R	Radial distance to reaction interface
R <sup>0</sup>	Radius of particle
s	sulfur content (wt. fraction)
S <sub>v</sub>	Volumetric space velocity (ft <sup>3</sup> /sec per ft <sup>3</sup> of bed)
S <sub>w</sub>	Weight space velocity (lb./hr. per lb. of char)
t	time (hr or sec)
U	Superficial velocity (ft per sec)
W	Bed weight (bm)
Y	Mole fraction H <sub>2</sub> S in the gas phase
ε	porosity
ρ	density
τ	tortuosity

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TABLE I

ANALYSIS OF CROWN CHAR		
	BEFORE TREATMENT	AFTER TREATMENT
<b>PROXIMATE, wt. %</b>		
MOISTURE	4.4	2.5
VM	<u>3.6</u>	<u>5.9</u>
FC	75.4	76.0
ASH	16.6	15.6
<b>ULTIMATE, wt. %, dry</b>		
C	76.8	
H	1.4	
N	1.2	
S	<u>3.1</u>	<u>1.5</u>
O	0.1	
ASH	17.4	

TABLE II

ANALYSIS OF CROWN CHAR FEED		
SIEVE SIZE, TYLER MESH	WT. % ON SIEVE	WT. % S IN FRACTION
28	39	2.57
48	34	2.59
100	20	3.14
200	6	3.80
PAN	1	—
<b>SULFUR SPECIES</b>		
ORGANIC		68 %
INORGANIC (PYRITIC)		29 %
SULFATE		3 %

TABLE III

**PHYSICAL PROPERTIES OF  
CROWN CHAR**

	BEFORE TREATMENT	AFTER TREATMENT
BULK DENSITY, lb/cu ft	20.7	20.7
PARTICLE DENSITY, gm/cc	1.08	1.01
PORE VOLUME, cc/gm	0.32	0.35
SURFACE AREA, M <sup>2</sup> /gm	123	114
MEAN MACRO- PORE DIAM., $\mu$	5	4.5

TABLE IV

**EFFECT OF H<sub>2</sub>S ON DESULFURIZATION  
AT 1600°F AND 115 PSIA**

INLET H <sub>2</sub> S, VOL %	REACTION TIME, HR.	PERCENT S REMAINING
0	1	12
0	2	22
1.6	2	72
3.2	1	118
3.2	2	105

TABLE V

**EFFECT OF PARTICLE SIZE  
ON DESULFURIZATION AT  
1600 °F, 15PSIA**

SIZE FRACT.	TIME, MIN.	SUPERFICIAL VELOCITY, ft/sec.	RESIDUAL SULFUR, % OF ORIG.
+ 28	5	0.53	68
- 200	5	0.51	66
+ 28	15	0.52	43
- 200	15	0.56	46
+ 28	10	0.22	65
- 200	10	0.19	72

TABLE VI

**DESULFURIZATION EXPERIMENTAL DESIGN**

	LOW	MID.	HIGH
PRESSURE, psia	15	30	60
SUPERFICIAL VEL, ft./sec.	0.5	1.0	2.0
VOLUMETRIC SPACE VEL, hr <sup>-1</sup>	11,150	22,300	44,600

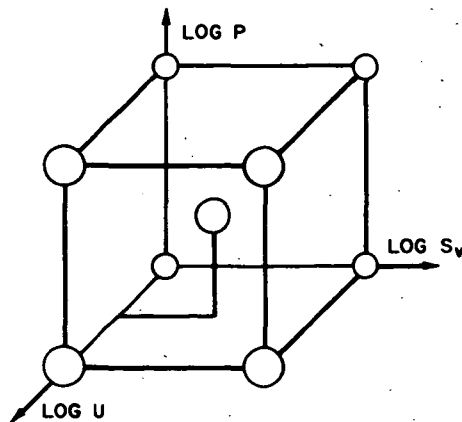


FIGURE 1

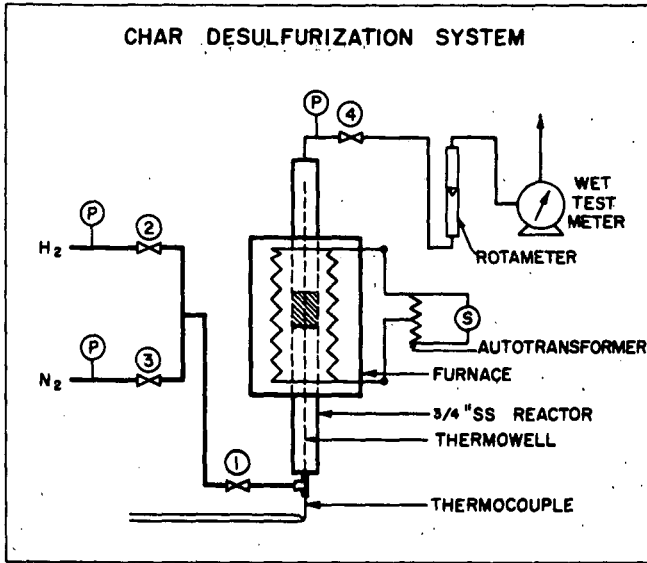
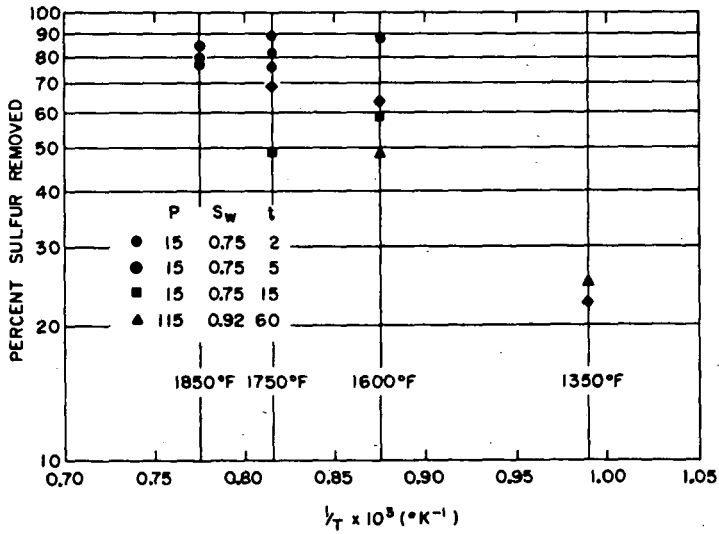


FIGURE 2

**EFFECT OF TEMPERATURE ON  
DESULFURIZATION**



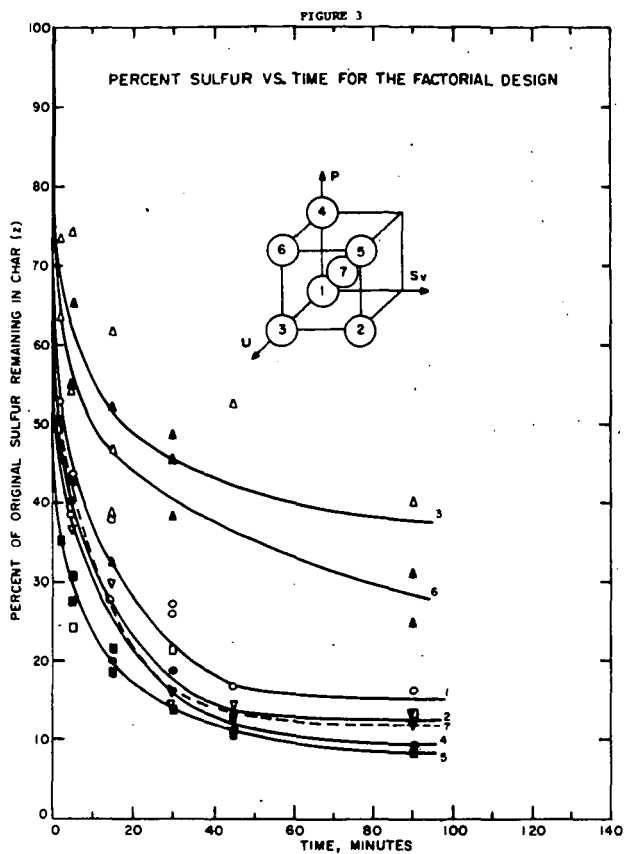


FIGURE 4  
INHIBITION ISOTHERMS FOR CHAR DESULFURIZATION

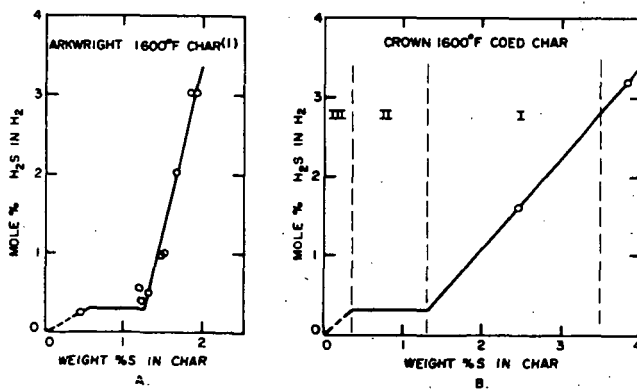


FIGURE 6

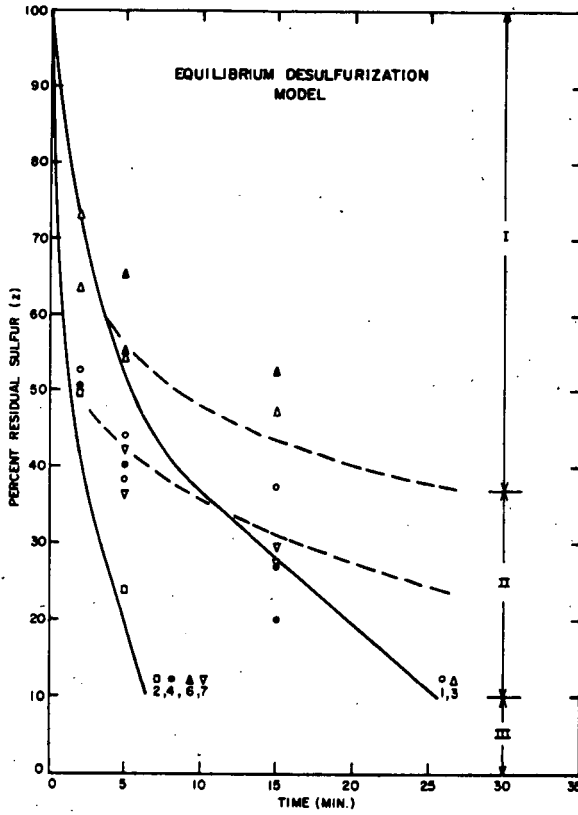
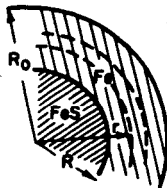


FIGURE 7

## PSEUDO STEADY-STATE DIFFUSION



$$-\frac{4\pi r^2 D}{r^2} \left( \frac{dC}{dr} \right) = N_s$$

At  $r = R,$

$$N_s = 4\pi R^2 \frac{dR}{d\theta} \left( \frac{\rho_{FeS}}{M_{FeS}} \right)$$



FIGURE 8

## DIFFUSION THROUGH A REACTED SHELL

$$\left(\frac{6MC_0D\epsilon}{\rho R_0^2 \tau^2}\right)t = 1 - \left(\frac{R}{R_0}\right)^2 \left[3 - 2\left(\frac{R}{R_0}\right)\right]$$

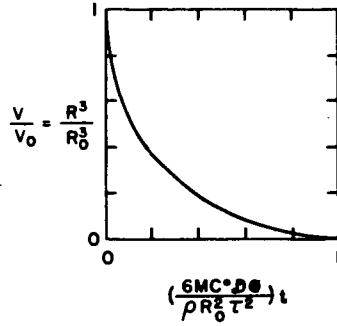


FIGURE 9

COMPARISON OF REAL AND HYPOTHETICAL  
DESULFURIZATION CURVES